



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 333 660
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 89810187.8

(51) Int. Cl.4: C 08 K 5/00

(22) Date of filing: 09.03.89

C 08 L 59/00
// (C08K5/00,5:13,5:20),
(C08K5/00,5:13,5:25)

(30) Priority: 18.03.88 US 170187

(71) Applicant: CIBA-GEIGY AG
Klybeckstrasse 141
CH-4002 Basel (CH)

(31) Date of publication of application:
20.09.89 Bulletin 89/38

(72) Inventor: Capocci, Gerald A.
25 Greenway Drive
Greenwich, CT 06431 (US)

(44) Designated Contracting States: DE FR GB IT NL

Zappia, Jean M.
3 Hollywood Street
Mohegan Lake, NY 10547 (US).

(54) Stabilization systems for polyacetals.

(57) A blend of a phenolic antioxidant and a hydrazine or oxamido derivative in appropriate proportions for use in stabilizing acetal homo- and copolymers against oxidative and thermal degradation.

EP 0 333 660 A2

Description

Stabilization Systems for Polyacetals

The instant invention pertains to an acetal homo- or copolymer composition comprising a hindered phenol and a specific hydrazine compound or oxamido compound, to a method of stabilizing acetal homo- or copolymers as well as to a method of reducing color formation in acetal homo- or copolymers which contain a hindered phenol.

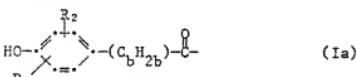
5 Polycetal homo- and copolymers are well known to those skilled in the art. These materials are a suitable replacement for metal in numerous applications as a result of properties such as high strength and stiffness, good fatigue life, excellent resilience and toughness, low moisture sensitivity, solvent resistance, excellent 10 electrical characteristics and the capability to maintain these properties at elevated temperatures. The molecular structure of the polymer is that of a linear acetal, consisting of unbranched polyoxymethylene chains of substantial length, generally averaging more than 1000 -CH₂O- units. The acetal homopolymers are, for example, prepared by the polymerization of anhydrous formaldehyde or by the polymerization of trioxane. Acetal copolymers are typified, for example, by the polymerization product of trioxane and a cyclic ether such 15 as ethylene oxide.

Since polyacetals are subject to oxidative and thermal degradation and discoloration, a wide variety of light 20 stabilizers and antioxidants have been recommended for use therein. Included among the latter are diverse hindered phenolic antioxidants as reflected for example in U.S. Patents 3,285,855, 3,644,482 and the like; as well as various hydrazine compounds as reflected for example in U.S. Patents 3,110,699 and 3,680,438. Although these groups of compounds have provided antioxidant properties to polyacetals, levels of discoloration during storage and exposure particularly with the hindered phenols have proven to be unacceptablely high for certain end uses. This potential deficiency is aggravated by the fact that the hindered phenol primary stabilizers are required in order to provide maximum thermal stability, the latter not being provided by the individual use of co-stabilizers even at higher concentration levels.

25 It has now been discovered that by including a special hydrazine or oxamido compound with a special hindered phenol in the proportions noted hereinafter as a stabilizing system for acetal homo- and copolymers, total stabilizing activity is achieved. Thus, the blend provides excellent stabilization against both oxidative and thermal degradation. Of primary importance, the combination provides significantly improved performance in the area where the individual hindered phenol is lacking, namely, in resistance to discoloration during storage 30 and/or exposure to environmental conditions. In fact, contrary to expectation, the use of higher levels of hindered phenol in such combinations does not result in a concomitant increase in discoloration of the acetal polymer.

35 As previously noted, the applicable hindered phenols and hydrazine or oxamido compounds are known to those skilled in the art and have been identified as antioxidants for use in acetal polymers. Various blends of the hindered phenol and hydrazine components have been identified for use as stabilizer systems for polyolefins, polyurethans and various elastomers. In addition, U.S. Patent 3,940,365 describes moulding compositions based on poly(oxymethylene) which contain a phenolic antioxidant and a specific compound having a nucleating effect. However, the unexpected performance pattern achieved with the use of the instant blends clearly provide a distinct situation.

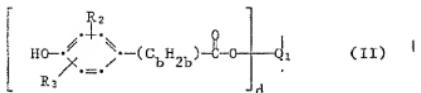
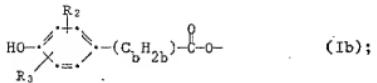
40 The instant invention pertains to an acetal homo- or copolymer which comprises
 (a) a hindered phenol corresponding to the formula I, II, III, IV, V, VI or VII,
 R₁X-(C₆H₄)_a-Q (I)
 wherein R₁ is a group of the formula Ia,



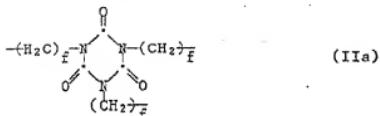
50 X is oxygen or sulfur, a is an integer from 6 to 30, preferably 6 to 18, b is an integer from 0 to 6, R₂ and R₃ are independently C₁-C₆alkyl, C₆-C₁₂cycloalkyl, phenyl or C₇-C₁₂arylalkyl, and R₂ is also hydrogen, Q is hydrogen or -A-(C₁H₂)-R₄. A is oxygen, sulfur or -N-

B

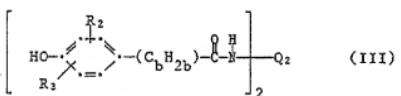
55 y is an integer from 2 to 20,
 B is C₁-C₄alkyl or C₁-C₄alkanoyl, and R₄ is hydrogen, hydroxy, C₁-C₄alkanoyloxy or a group of the formula Ib.



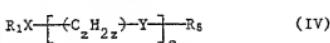
wherein R₂, R₃ and b are as defined above, d is an integer from 2 to 6, and Q₁ is a d-valent aliphatic hydrocarbon of 1 to 18 carbon atoms, a d-valent aromatic or aromatic aliphatic hydrocarbon of 6 to 20 carbon atoms or a group of the formula IIa



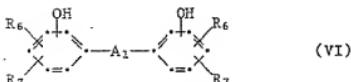
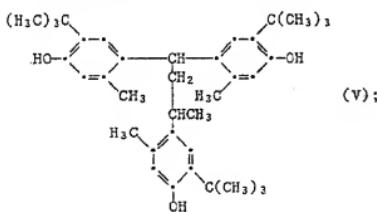
wherein f is an integer from 1 to 4:



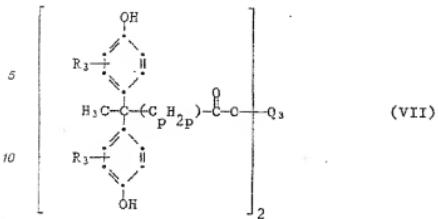
wherein R₂, R₃ and b are as defined above, and Q₂ is C₁-C₁₈alkylene;



wherein R₁ and X are as defined above, z is an integer from 2 to 6, e is an integer from 3 to 40, preferably 3 to 10, Y is oxygen or sulfur, and R₅ is hydrogen, C₁-C₄alkyl or a group of the formula Ia:

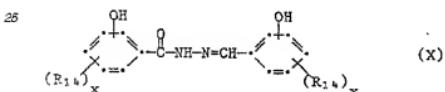


wherein R₆ and R₇ are independently C₁-C₁₈alkyl, C₅-C₁₂cycloalkyl, phenyl or C₇-C₉aralkyl, and R₈ is also hydrogen, and A₁ is a group $\text{C}(\text{R}_8)_2$, wherein R₈ and R₉ are independently hydrogen or C₁-C₁₈alkyl;

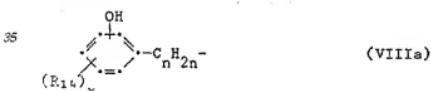


75 wherein R₃ is as defined above, p is 1 or 2 and Q₃ is C₂-C₁₀alkylene; and

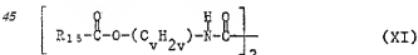
(b) a hydrazine compound corresponding to the formula VIII, IX or X



wherein R₁₂ and R₁₃ are independently C₁-C₁₈alkyl, C₁-C₁₈alkyloxy, phenyl, C₇-C₁₈aralkyl or a group of the formula VIII.



40 Z is a direct bond, C₁-C₁₈alkylene or phenylene, the radicals R₁₄ are independently C₁-C₁₈alkyl, C₅-C₁₂cycloalkyl, phenyl or C₇-C₁₈aralkyl, w is 0 or 1, x is an integer from 0 to 4 and n is an integer from 0 to 6, with the proviso that x is different from zero, when w is 1; or
 (c) an oxamido compound of the formula XI



50 wherein R₁₅ is C₁-C₁₈alkyl, phenyl, C₇-C₁₈aralkyl or a group of the formula VIIIa and v is an integer from 0 to 6, preferably 1 to 6, in particular 2 to 6; the weight ratio of the components (a):(b) or (a):(c) is 20:1 to 1:10. Alkyl is for example methyl, ethyl, propyl, n-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, 1,1,3,3-tetramethylbutyl, nonyl, decyl, undecyl, dodecyl or octadecyl.

C₁-C₁₈alkyloxy is for example methoxy, ethoxy, propoxy, n-butoxy, tert-butoxy, pentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy or octadecyloxy.

55 C₁-C₄alkanoyl is for example acetyl, propionyl or butyryl.

C₁-C₄alkanoyloxy is for example acetyloxy, propionyloxy or butyryloxy.

C₅-C₁₂cycloalkyl is for example cyclopentyl, cyclohexyl or cyclooctyl. Cyclohexyl is preferred.

C₇-C₈aralkyl is in particular C₇-C₈phenylalkyl, for example benzyl, α -methylbenzyl, α,α -dimethylbenzyl or phenylethyl. Benzyl is preferred.

⁶⁰ C₁-C₁₈alkylene is for example methylene, dimethylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, decamethylene, dodecamethylene or octadecamethylene.

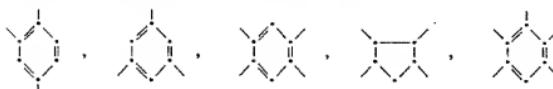
For compounds of formula II, Q₁ as a bivalent hydrocarbon can be e.g. straight-chain or branched C₂-C₁₀alkylene or C₂-C₆alkylidene such as, for example ethylene, ethyldiene, trimethylene, tetramethylene,

65 pentamethylene, 2,2-dimethylpropane-1,3-diyl, hexamethylene, heptamethylene, octamethylene, decamethylene, 2,2-pentamethylene-propane-1,3-diyl and cyclohexylene or C₆-C₁₀ arylene such as, for example,

methylene, 1,2-pentamethylene, μ -Spano-1,3-dienyl, and cyclonexylene or C₈-C₁₀arylene such as, for example,

phenylene, phenylene substituted by one or more C₁-C₄alkyl, or naphthylene.

Q₁ as a trivalent, tetravalent or pentavalent hydrocarbon can be e.g. a group of the following formulae

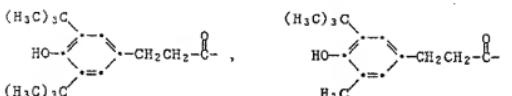


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or alkanetriyl of 3 to 6 carbon atoms, such as e.g. glyceryl or trimethylpropylene or alkanetetrayl of 4 to 6 carbon atoms such as e.g. pentaerythryl.

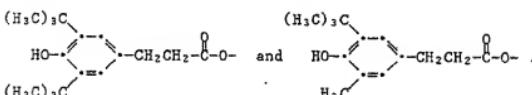
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Formula Ia represents preferably one of the following groups:



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Formula Ib is in particular one of the groups



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In the group of the formula IIa f is preferably 2.

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Those compositions are preferred, wherein component (a) is a compound of the formula I, II, III, IV, V or VI, in particular I, II, III or IV.

Z is preferably a direct bond or C₁-C₆alkylene.

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Compounds of formula I which are preferred exhibit X as oxygen, b as an integer from 0 to 2, R₂ and R₃ as alkyl of 1 to 8 carbon atoms, A as oxygen, b as 2, R₄ as hydrogen or a group of the formula Ib. Particularly preferred are those compounds wherein R₂ and R₃ are tert-butyl positioned ortho to the hydroxyl group and b is 2. A specific compound of preference is octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate.

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Compounds of formula II which are preferred exhibit R₂ and R₃ as C₁-C₆-alkyl, in particular tert-butyl positioned ortho to the hydroxyl group, b as 2, d as 2 or 4 and Q₁ as C₂-C₆alkylene or pentaerythryl. Specific compounds of preference are 1,6-hexamethylene bis[3'(3',5'-di-tert-butyl-4'-hydroxyhydrocinnamate] and tetraakis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane.

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Compounds of formula III which are preferred exhibit R₂ and R₃ as C₁-C₆alkyl and preferably tert-butyl positioned ortho to the hydroxyl group, b as 2 and Q₂ as C₂-C₆alkylene. The specific compound of preference is N,N'-hexamethylene bis[3,5-di-tert-butyl-4-hydroxyhydrocinnamide].

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Compounds of formula IV which are preferred exhibit X and Y as oxygen, b as an integer from 0 to 2, R₂ and R₃ as alkyl of 1 to 8 carbon atoms, z as 2, e as an integer from 3 to 20, and R₄ as a group of the formula Ia. Particularly preferred are those compounds wherein R₂ and R₃ are tert-butyl positioned ortho to the hydroxyl group. A specific compound of preference is triethylene glycol bis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)-propionate].

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Compounds of formula VI which are preferred exhibit R₆ and R₇ as methyl or tert-butyl and R₈ and R₉ as hydrogen or methyl. Specific compounds of preference are bis[2-hydroxy-3-tert-butyl-5-methylphenyl]methane and 1,1-bis[2'-hydroxy-3',5'-di-tert-butylphenyl]ethane.

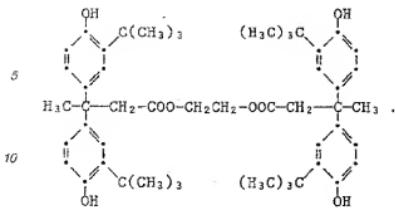
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A preferred compound of formula VII is

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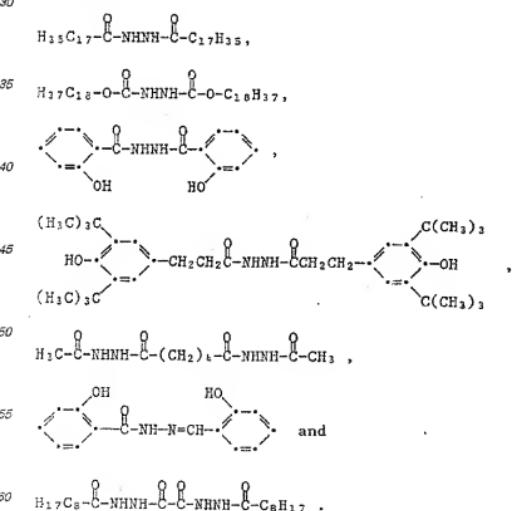
Preferred compositions of the invention are those wherein component (a) is octadecyl 3-[3'(5'-di-tert-butyl-4-hydroxyphenyl)propionate, 1,6-hexamethylene bis[3-(5'-di-tert-butyl-4'-hydroxyhydrocinnamate], tetrakis-[methylene 3-(3'-5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane, N,N'-hexamethylene bis[3-(5-di-tert-butyl-4-hydroxyhydrocinnamamide] or triethylene glycol bis[3-(3'-5'-di-tert-butyl-4'-hydroxyphenyl)propionate].

According to a further preferred embodiment in component (b) R_{12} and R_{13} are independently C_1 - C_{18} alkyl or a group of formula V_3 , Z_3 is a direct bond or C_1 - C_8 alkylene and the radicals R_{14} are independently C_4 - C_{18} alkyl, C_6 - C_{18} cycloalkyl, phenyl or benzyl.

Preferred groups of the formula VIIia and preferred compounds of the formula X are those wherein the OH group is either in the ortho- or para-position. When the OH group is in the para-position, the groups of the formula VIIia preferably contain two R_1 radicals positioned ortho to the hydroxyl group, which are alkyl of 4 to 8 carbon atoms and, most preferably, tert-butyl.

With respect to compounds of formula X, the OH group is preferably in the ortho-position to the linking chain.

Representative compounds of component (b) include



Another preferred composition of the instant invention contains as component (a) 1,6-hexamethylene bis[3',5'-di-*t*-butyl-4'-hydroxyhydrocinnamate] and as component (b) N,N'-bis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionyl]hydrazine. The combination of these components particularly reveals a performance-

improvement in the hindered phenol.

Preferred compositions are also those which contain components (a) and (c).

In compounds of the formula XI R₁₆ is preferably a group of the formula VIIa with the OH radical in the para-position and two R₁₄ groups positioned ortho to the hydroxyl group, R₁₄ being preferably tert-butyl. A representative compound is 2,2'-oxamido-bis[ethyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate] (%NAU-GARD XL-1 from Uniroyal).

Methods for preparing the compounds of component (a) are well known to those skilled in the art. Specific reference is made to U.S. Pat. Nos. 3,285,855, 3,531,483, 3,584,047, 3,632,553, 3,644,482, 3,944,594, 4,032,562 and 4,507,420 for information regarding the phenols of formula I-V and VI and their methods of preparation. The compound of formula V is %TOPANOL CA available from ICI Corp. The compounds of formula VII can be prepared as described, for example, in U.S. Patent 3,960,928.

The compounds of component (b) and methods for their preparation are disclosed in U.S. Pat. Nos. 3,110,696 and 3,660,436, said disclosures being fully incorporated herein.

In general, the blends of the present invention are employed in from about 0.01 to about 10% by weight of the stabilized composition, although this will vary with the particular application. An advantageous range is from about 0.05 to about 2%, and especially 0.1 to about 1%. The weight ratio of component (a) to component (b) or component (c) will generally range from 20:1 to 1:10, preferably 9:1 to 1:9, and most preferably 2:3:1.

The stabilizers of the instant invention, either individually or in combination, may readily be incorporated into the acetal polymers by conventional techniques, at any convenient stage prior to the manufacture of shaped articles therefrom. For example, the stabilizers may be mixed with the polymer in dry powder form, or a suspension or emulsion of the stabilizer may be mixed with a solution, suspension, or emulsion of the polymer. The resulting stabilized polymer compositions of the invention may optionally also contain various conventional additives. Included among these additives are basic co-stabilizers such as calcium citrate, melamine, cyanoguanidine, polyamides, alkali and alkaline earth metal salts of high fatty acids, and amines; phosphites and phosphonites; peroxide-destroying compounds such as esters of thioldipropionic acid; and the like.

The instant invention also relates to a method of stabilizing an acetal homo- or copolymer against thermal or oxidative degradation, which comprises incorporating into said acetal components (a) and (b) or (a) and (c) as defined above.

Another embodiment of the instant invention is a method of reducing color formation in acetal homo- or copolymers containing a hindered phenol (component (a)), which comprises incorporating into said acetal homo- or copolymers component (b) or (c) as defined above.

The following examples illustrate the embodiments of this invention.

Test compounds

- A - 1,6-hexamethylene bis[3',5'-di-tert-butyl-4'-hydroxyhydrocinnamate]
- B - triethylene glycol bis[3-tert-butyl-5-methyl-4-hydroxyphenyl]propionate
- C - tetrakis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane
- D - N,N'-hexamethylene bis[3,5-di-tert-butyl-4-hydroxyhydrocinnamide]
- E - octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate
- F - 1,3,5-tris[3',5'-di-tert-butyl-4'-hydroxybenzoyloxyethyl]isocyanurate
- G - 1,1,3-tris[3'-tert-butyl-4'-hydroxy-5'-methyl(phenyl)]butane
- H - 1,1-bis[3'-tert-butyl-4'-hydroxy-5'-methyl(phenyl)]butane
- J - N,N'-bis[β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl]hydrazine
- K - 2,2'-oxamido-bis[ethyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]

Example 1:

The additives in the indicated concentrations are dry blended into polyoxymethylene resin [trioxane-ethylene oxide copolymer (%CELCON from Celanese) with base stabilization system of 0.2% bis-stearamide and 0.1% calcium hydroxystearate] and extruder compounded (single extrusion) into pellets at 185°C. The pellets are stored in a dark area in glass petri dishes at ambient temperatures for the indicated time periods and specimen yellowness index (YI) is determined according to ASTM D 1925.

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	Components	Conc. (% by wt.)	Yellowness Index		
			Initial	64 Days	131 Days
5	A	0.5	3.6	10.4	11.3
	J	0.5	3.6	2.7	2.3
10	A/J	0.25/0.25	2.0	1.5	1.3
	A/J	0.3/0.2	1.5	1.2	1.2
15	A/J	0.35/0.15	2.3	2.0	1.8
	A/J	0.4/0.1	1.9	1.5	1.4
20	A/J	0.45/0.05	1.4	1.2	1.5
	A/J	0.475/0.025	1.2	1.0	1.0
25	A/J	0.2/0.3	1.0	1.4	1.3
	A/J	0.15/0.35	2.6	1.8	1.6
30	A/J	0.1/0.4	2.7	2.1	2.0
	A/J	0.05/0.45	2.2	1.7	1.6
35	K	0.5	1.7	1.7	2.0
	A/K	0.25/0.25	1.0	1.9	2.1
40	A/K	0.35/0.15	1.4	2.8	3.2
	A/K	0.45/0.05	1.7	3.0	3.4
45	A/K	0.15/0.35	1.6	2.3	2.6
	A/K	0.05/0.45	1.4	2.0	2.4
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<u>COSTA-BILIZER 0.3 %</u>	<u>Oven aging at 80° C ΔYI at 20 Weeks</u>	<u>Storage in Water at 70° C YI at 20 Weeks</u>	
0.3 % A	18.7	33.4	5
0.3 % A + 0.01 % J	13.1	17.3	
0.3 % A + 0.03 % J	12.0	14.7	
0.3 % A + 0.05 % J	12.8	13.0	10
<u>COSTA-BILIZER 0.15 % Ca CITRATE</u>			15
0.3 % A	18.0	10.2	
0.3 % A + 0.01 % J	13.1	8.3	
0.3 % A + 0.03 % J	14.5	8.6	20
0.3 % A + 0.05 % J	12.5	8.2	
<u>COSTA-BILIZER 0.3 % MELAMINE</u>			25
0.3 % A	10.6	9.8	
0.3 % A + 0.01 % J	9.0	7.5	
0.3 % A + 0.03 % J	8.1	9.0	30
0.3 % A + 0.05 % J	8.1	8.3	
<u>COSTA-BILIZER 0.3 % CYANOGUANIDINE</u>			35
0.3 % A	10.5	16.4	
0.3 % A + 0.01 % J	9.0	7.2	40
0.3 % A + 0.03 % J	10.2	7.3	
0.3 % A + 0.05 % J	10.1	6.0	45

Example III:

Example I is repeated utilizing a variety of phenolic antioxidants.

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	<u>Additive</u>	<u>Conc. (% by wt.)</u>	<u>YI Initial</u>	<u>YI 45 Days</u>
5	A	0.5	4.0	16.2
	A/J	0.4/0.1	4.1	5.0
	B	0.5	3.8	4.0
	B/J	0.4/0.1	2.2	2.8
	C	0.5	3.8	13.0
10	C/J	0.4/0.1	2.5	4.0
	D	0.5	3.0	8.0
	D/J	0.4/0.1	3.0	4.1
	E	0.5	4.1	26.6
	E/J	0.4/0.1	5.5	7.2
15	F	0.5	9.2	14.5
	F/J	0.4/0.1	8.5	11.1
	G	0.5	11.1	14.9
	G/J	0.4/0.1	5.4	7.2
	H	0.5	12.0	21.8
20	H/J	0.4/0.1	5.6	7.0
	J	0.5	4.1	5.3

25 Example IV:

Example III is repeated with the exception that the resulting samples are subjected to oven aging for five days at 110°C.

	<u>Additive</u>	<u>Conc. (% by wt.)</u>	<u>YI - Oven Aged</u>
30	C	0.5	23.3
	C/J	0.475/0.025	17.7
	E	0.5	23.2
35	E/J	0.475/0.025	13.3
	F	0.5	39.7
	F/J	0.475/0.025	25.9
	J	0.5	26.3

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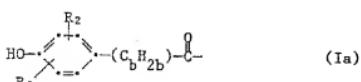
It is thus seen that the instant combination of antioxidants provides significantly improved stabilization effectiveness in acetal polymers. This improvement is particularly evident in a key indicia of stabilization, namely, resistance to discoloration.

45 In summary, this invention provides antioxidant systems for stabilizing acetal polymers against oxidative and thermal degradation. Variations may be made in various elements thereof without departing from the scope of the invention as defined by the following claims.

Claims

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1. An acetal homo- or copolymer which comprises
 (a) a hindered phenol corresponding to the formula I, II, III, IV, V, VI or VII,
 $R_1X-(C_6H_{2n})_Q$ (I)
 wherein R_1 is a group of the formula Ia,

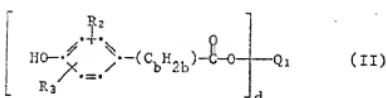
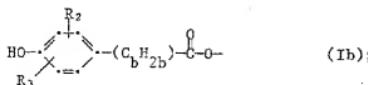


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X is oxygen or sulfur, a is an integer from 8 to 30, b is an integer from 0 to 6, R_2 and R_3 are independently $\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_5\text{-C}_{12}$ cycloalkyl, phenyl or $\text{C}_7\text{-C}_{16}$ aralkyl, and R_2 is also hydrogen, Q is hydrogen or $-A(C_6H_{2n})-R_4$, A is oxygen, sulfur or $\text{--}\overset{\text{B}}{\underset{\text{B}}{\text{--}}}$.

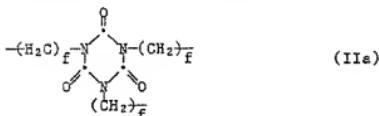
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y is an integer from 2 to 20,
 B is C₁-C₄alkyl or C₁-C₄alkanoyl, and R₄ is hydrogen, hydroxy, C₁-C₄alkanoyloxy or a group of the formula Ib,

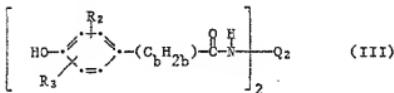


wherein R₂, R₃ and b are as defined above, d is an integer from 2 to 6, and Q₁ is a d-valent aliphatic hydrocarbon of 1 to 16 carbon atoms, a d-valent aromatic or aromatic aliphatic hydrocarbon of 6 to 20 carbon atoms or a group of the formula IIa

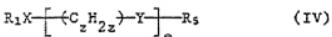
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wherein f is an integer from 1 to 4;

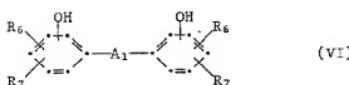
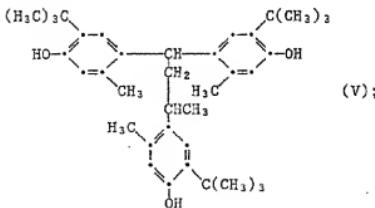


wherein R₂, R₃ and b are as defined above, and Q₂ is C₁-C₄alkylene;

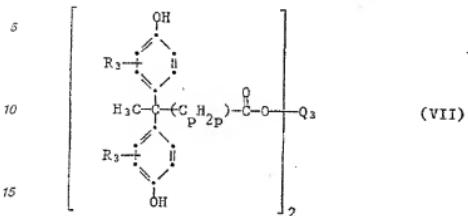


wherein R₁ and X are as defined above, z is an integer from 2 to 6, e is an integer from 3 to 40, Y is oxygen or sulfur, and R₆ is hydrogen, C₁-C₄alkyl or a group of the formula Ia;

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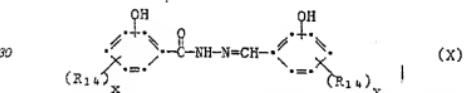
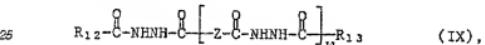
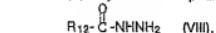
wherein R₆ and R₇ are independently C₁-C₁₈alkyl, C₆-C₁₂cycloalkyl, phenyl or C₁-C₆aralkyl, and R₈ is also hydrogen, and A₁ is a group $\text{C}(\text{R}_8)_2$, wherein R₈ and R₉ are independently hydrogen or C₁-C₆alkyl;



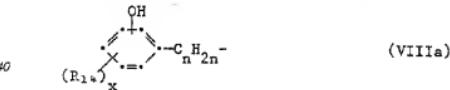
wherein R₈ is as defined above, p is 1 or 2 and Q₃ is C₂-C₁₀alkylene; and

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(b) a hydrazine compound corresponding to the formula VIII, IX or X

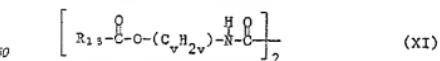


wherein R₁₂ and R₁₃ are independently C₁-C₁₈alkyl, C₁-C₆alkyloxy, phenyl, C₁-C₆aralkyl or a group of the formula VIIa,



Z is a direct bond, C₁-C₆alkylene or phenylene, the radicals R₁₄ are independently C₁-C₁₈alkyl, C₆-C₁₂cycloalkyl, phenyl or C₁-C₆aralkyl, w is 0 or 1, x is an integer from 0 to 4 and n is an integer from 0 to 6, with the proviso that x is different from zero, when w is 1; or

(c) an oxamido compound of the formula XI



wherein R₁₅ is C₁-C₁₈alkyl, phenyl, C₁-C₆aralkyl or a group of the formula VIIa and v is an integer from 0 to 6; the weight ratio of the components (a):(b) or (a):(c) is 20:1 to 1:10.

2. The composition of claim 1, wherein said hindered phenol corresponds to the formula I, II, III, IV, V or VI,

3. The composition of claim 1, wherein said hindered phenol corresponds to formula I.

4. The composition of claim 1, wherein said hindered phenol corresponds to formula I and X is oxygen, b is an integer from 0 to 2, R₂ and R₃ are independently C₁-C₆alkyl, A is oxygen, y is 2 and R₄ is hydrogen or a group of the formula Ib.

5. The composition of claim 4, wherein R₂ and R₃ are tert-butyl positioned ortho to the hydroxyl group and b is 2.

6. The composition of claim 1, wherein said hindered phenol corresponds to formula II.

7. The composition of claim 1, wherein said hindered phenol corresponds to formula II and R₂ and R₃ are independently C₁-C₆alkyl, b is 2, d is 2 or 4 and Q₁ is C₂-C₁₈alkylene or pentaerythrityl.

8. The composition of claim 1, wherein said hindered phenol corresponds to formula III.

9. The composition of claim 1, wherein said hindered phenol corresponds to formula III and R₂ and R₃ are independently C₁-C₆alkyl, b is 2 and Q₂ is C₂-C₆alkylene.

10. The composition of claim 1, wherein said hindered phenol corresponds to formula IV.

11. The composition of claim 1, wherein said hindered phenol corresponds to formula IV and X and Y are oxygen, b is an integer from 0 to 2, R₂ and R₃ are independently C₁-C₆alkyl, z is 2, e is an integer from 3 to 20 and R₅ is a group of the formula Ia.

12. The composition of claim 11, wherein R₂ and R₃ are tert-butyl positioned ortho to the hydroxyl group.

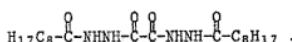
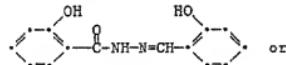
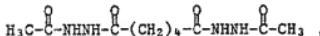
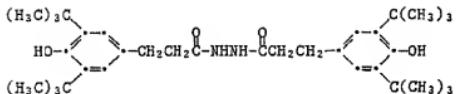
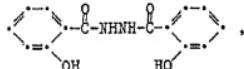
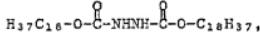
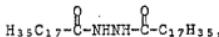
13. The composition of claim 1, wherein said hindered phenol is octa[acetyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)proponate, 1,6-hexamethylene bis[3'(3',5'-di-tert-butyl-4'-hydroxyhydrocinnamate], tetrakis-[methylenne 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)proponate]methane, N,N'-hexamethylene bis[3,5-di-tert-butyl-4-hydroxyhydrocinnamamide] or triethylene glycol bis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)proponate].

14. The composition of claim 1, wherein in component (b) R₁₂ and R₁₃ are independently C₁-C₆alkyl or a group of formula VIIa, Z is a direct bond or C₁-C₆alkylene and the radicals R₁₄ are independently C₂-C₆alkyl, C₅-C₆cycloalkyl, phenyl or benzyl.

15. The composition of claim 14, wherein the OH in the group of the formula VIIa and in the compounds of formula (X) is positioned either in the 2- or 4-position.

16. The composition of claim 15, wherein the OH in the group of the formula VIIa is in the para-position, x is 2 and each R₁₄ is tert-butyl positioned ortho to the OH group.

17. The composition of claim 1, wherein said hydrazine is



18. The composition of claim 1, wherein said hindered phenol is 1,6-hexamethylene bis[3,5-di-tert-butyl-4-hydroxyhydrocinnamate] and said hydrazine compound is N,N'-bis[β-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionyl]hydrazine.

19. The composition of claim 1 comprising components (a) and (c).

20. The composition of claim 19, wherein component (c) is 2,2'-oxamido-bis[ethyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)proponate].

21. The composition of claim 1 which additionally contains a basic co-stabilizer selected from the group consisting of calcium citrate, melamine, cyanoguanidine, polyamides, alkali and alkaline earth metal salts of fatty acids, amines, phosphites, phosphonites and peroxide-destroying compounds.

22. A method of stabilizing an acetal homo- or copolymer against thermal or oxidative degradation,

which comprises incorporating into said acetal components (a) and (b) or (a) and (c) according to claim 1.
23. A method of reducing color formation in acetal homo- or copolymers containing component (a) according to claim 1, which comprises incorporating into said acetal homo- or copolymers component (b) or (c) as defined in claim 1.

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(11) Publication number:

0 333 660 A3

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EUROPEAN PATENT APPLICATION

(21) Application number: 89810187.8

⑤ Int. Cl.^s: C08K 5/00, C08L 59/00,
//C08K5/00,5:13,5:20),
(C08K5/00,5:13,5:25)

㉙ Date of filing: 09.03.89

② Priority 18.03.88 116 130187

(4) Date of publication of application:
20.09.89 Bulletin 89/38

Designated Contracting States
DE FR GB IT NL

⑧ Date of deferred publication of the search report:
24.07.91 Bulletin 91/30

⑦ Applicant: CIBA-GEIGY AG
Klybeckstrasse 141
CH-4002 Basel(CH)

(7) Inventor: Capocci, Gerald A.
25 Greenway Drive
Greenwich, CT 06431(US)
Inventor: Zappia, Jean M.
3 Hollywood Street
Mohegan Lake, NY 10547(US)

54 Stabilization systems for polyacetals.

(v) A blend of a phenolic antioxidant and a hydrazine or oxamido derivative in appropriate proportions for use in stabilizing acetal homo- and copolymers against oxidative and thermal degradation.

EP 0 333 660 A3

EUROPEAN SEARCH
REPORT

EP 89 81 0187

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.s)
A	DE-B-2 540 206 (DEGUSSA) * claim *	1-23	C 08 K 5/00 C 08 L 59/00 // (C 08 K 5/00 C 08 K 5 C 08 K 13
A,D	US-A-3 660 438 (M. DEXTER) * example 18 *	1-23	C 08 K 5/20 (C 08 K 5/00 C 08 K)
A	US-A-3 152 101 (T. DOLCE) * claims *	1-23	C 08 K 5/20 (C 08 K 5/00 C 08 K)
A	DE-A-2 203 836 (CIBA-GEIGY AG) * claims; page 7, lines 11-14 *	1-23	C 08 K 5/13 C 08 K C 08 K 5/25)
TECHNICAL FIELDS SEARCHED (Int. Cl.s)			
C 08 K C 08 L			
The present search report has been drawn up for all claims			
Place of search	Date of compilation of search	Examiner	
The Hague	24 May 91	HOFFMANN K.W.	
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T:	theory or principle underlying the invention		